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Impact of Several Chemical and Physical Properties of Two H-Coal Recycle Solvent Streams on Their Relative Solvent Quality

Joe Collins

IMPACT OF SEVERAL CHEMICAL AND PHYSICAL PROPERTIES OF TWO H-COAL RECYCLE SOLVENT STREAMS ON THEIR RELATIVE SOLVENT QUALITY

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Presented to

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In Partial Fulfillment

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Master of Science

by

Joe T. Collins

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THEIR RELATIVE SOLVENT QUALITY

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

IMPACT OF SEVERAL CHEMICAL AND PHYSICAL PROPERTIES
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THEIR RELATIVE SOLVENT QUALITY

Joe T. Collins August 1984 66 pages
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The purpose of this study was to follow the solvent quality curve of the recycle solvent streams of the H-Coal Pilot Plant run by Ashland Petroleum Compnay at Catlettsburg, Kentucky. This was done with the use of a microautoclave (shaker-bomb liquefaction unit). Several physical and chemical properties of these recycle oils were determined, and these values were correlated with the observed solvent quality. It is shown that the relative, solvent quality of these recycle oils correlate well with many of the chemical and some of the physical properties determined in this study.

I. INTRODUCTION

Coal is an abundant resource which has yet to reach its full potential as a replacement for energy needs now met by petroleum. Although coal can be used in its natural form to replace petroleum in some instances, such as conversion to coal fired boilers for heating or coal fired turbines to produce electricity, substitution is not feasible in many operations due to coal's solid form. To achieve usage as a fuel, and perhaps as a chemical feedstock, some type of a method must be devised to convert the coal into a liquid form. This task, and the understanding of the processes involved in the liquefaction of coal, has proved to be formidable, involving input from many fields of science.

As a starting point, let us examine the structure of coal. It has been described as "an amorphous, cross-linked layered polymeric structure. Condensed aromatic ring systems of high molecular weight, containing small quantities of sulfur, oxygen, and nitrogen as heteroatomic species, comprise a significant portion of this macromolecule. The cross-linking is provided by relatively weak bonds such as methylene, sulfide, disulfide or ether linkages."[1] This description gives a reasonable idea of the structure of the coal matrix. The model molecule in Figure I[2] shows many examples of the possible bonds and ring formations found in coal, but is not

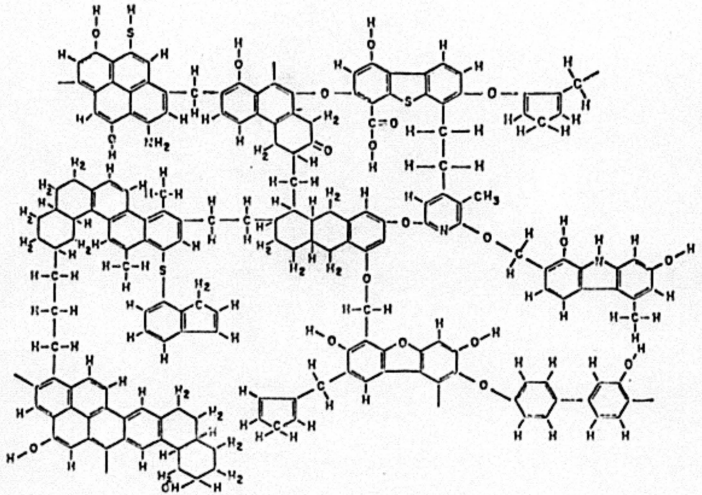


Figure I. Wiser Model for the Bituminous Coal Matrix[2]

meant to suggest an actual isolated coal "molecule." As yet there has been no specific structure determined for the chemical make-up of the complex coal matrix.

The reactions of the coal matrix during liquefaction have been under study for some time. An understanding of the basic coal liquefaction process is necessary before any comprehensive study of coal liquefaction may be undertaken. This process can easentially be broken into two steps. The first step in coal liquefaction is the thermal cleavage of some of the above mentioned bridging linkages, producing radicals. As shown in Table 1,[3] the bonds that are thermally cleaved are specific only as to the type of bond broken. The location of the bond in the coal matrix is not a significant factor.

The next step in coal liquefaction is the capping of the thermally produced radicals to prevent char formation. A schematic representation of this can be seen in Figure II.[4] This schematic shows what happens both with and without the presence of a hydrogen source. The yield of lighter fragments is increased by the addition of hydrogen. This capping of the thermally cleaved coal fragments can be achieved in two ways. One is the direct hydrogenation of the radicals by an atmosphere of hydrogen. The other is the use of a hydrogen donating solvent. At this time the most efficient coal liquefaction schemes use a hydrogen donor solvent for stabilizing the radicals produced thermally.

Table 1[3]

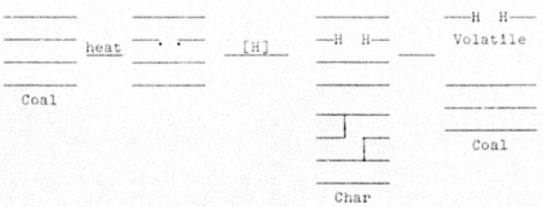
Some Representative Bond Dissociation Energies

Compound	Bond Dissociation Energy (Kcal/mole)	Half-life at 450°C a,b
C_6H_5--C_6H_5	103	301.5×10^6 yrs
RCH_2CH_2--CH_2CH_2R	83	271.1 yrs
C_6H_5--$CH_2C_6H_5$	81	67.4 yrs
RCH_2--OCH_2R	80	33.6 yrs
$C_6H_5CH_2$--CH_3	72	46.8 days
$C_6H_5CH_2$--$CH_2CH_2C_6H_5$	69	5.8 days
$C_6H_5CH_2$--OCH_3	66	17.2 hrs
$C_6H_5CH_2$--$CH_2C_6H_5$	57	1.97 min
$C_6H_5CH_2$--$OCH_2C_6H_5$	56	58.9 sec
$C_6H_5CH_2$--OC_6H_5	51	1.6 sec
$C_6H_5CH_2$--SCH_3	51	1.8 sec
CH_2=$CHCH_2$--CH_2CH=CH_2	38	2.1×10^{-4} sec
$(C_6H_5)_3C$--$C(C_6H_5)_3$	11	1.5×10^{-12} sec

[a] $k = 10^{15} e^{-BDE/RT}$

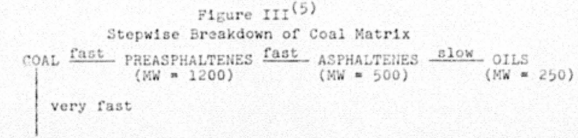
[b] $t_{\frac{1}{2}} = 0.693/k$

Figure II[4]
Schematic of Radical Capping



As the coal is liquefied, it is generally agreed that the first products formed are the preasphaltenes, which are very large molecules. Next the asphaltenes are formed, either from the coal matrix directly or from a breakdown of the preasphaltenes. After the asphaltenes, an oil yield is obtained, both from a breakdown of the asphaltenes and directly from the coal as it is first heated. The small amount of oil formed as the coal is first heated may have been in the micropore system of the coal matrix. Figure III[5] shows this process as a step-wise reaction. Although these classes of coal-derived compounds may be differentiated by molecular weight, the most common classification method is by solubility.[6]

Figure III[5]
Stepwise Breakdown of Coal Matrix



The product distribution of the final product from a coal liquefaction process is dependent upon many variables. Some of these include reactor temperature, pressure, and residence time as well as interrelationships between the amounts of coal, catalyst (if any), type of solvent, and available hydrogen.[7] In addition to this, the properties of a coal liquid are also related to the parent coal.[8] A coal liquid, in the context of this thesis, is a liquid derived from the thermal breakdown of the coal matrix. Hydrogen will have been added during this breakdown to stabilize the coal matrix fragments as they are formed.

To make a coal conversion plant feasible the hydrogen donor solvent should be derived from the product produced from the liquefaction of coal. In this way the plant can maintain solvent balance except for an outside source of solvent for startup purposes. As part of the product, this solvent, called the recycle solvent, is subject to the same reactor conditions as the overall product. In fact, many of the reactor conditions are transmitted to the coal through the recycle solvent due to the many roles the solvent plays. Some of the roles include a carrier for the coal particles to the reactor, a heat transfer agent, a hydrogen donor to the radicals formed, a solvent for the newly formed products and a carrier of wastes (ash, coal fines, catalysts particles, etc.) from the reactor.[9]

Another important role of the recycle solvent is product upgrading by increasing the hydrogen content of the product as well as removal of a portion of the heteroatoms (S, N, O) that are present.[10] Both of these processes are achieved

by the addition of hydrogen to the coal matrix, or through the addition of hydrogen to the product molecules derived from the coal matrix. This is achieved mainly by the recycle solvent. As the hydrogen is added, it may split out the heteroatoms. Unfortunately, the heteroatom removal uses large amounts of hydrogen, with little of it actually contained in the final liquid product. This added hydrogen is beneficial in producing a lighter (lower boiling) product. Also, the amount of available hydrogen in the recycle solvent is increased, hence increasing the amount of hydrogen available that may be added to the coal matrix and/or the product molecules.

There are several processes now undergoing evaluation for possible commercial use. The main three that yield a liquid product directly are the Exxon Donor Solvent (EDS) process, the Solvent Refined Coal II (SRC II) process, and the H-Coal process.[11] As shown in Table 2,[12] there are differences in the operating parameters of these processes, and these differences are reflected in the product distribution as well as the characteristics of the recycle solvent.

Table 2[12]

Reaction Parameters

Liquefaction Process	Temp.	Hydrogen Pressure	Process Catalyst
Exxon Donor Solvent	450°C	12.2 MPa	None
Solvent Refined Coal II	450°C	14.3 MPa	None
H-Coal	450°C	20.3 MPa	Co/Mo on Alumina

The EDS process has the distinction of separating the coal liquefaction step from the product and recycle solvent catalytic upgrading step. This separation allows optimizing of both steps. The EDS process appears very sensitive to the quality of the recycle solvent;[13] therefore the hydrogenation of the solvent is closely controlled. The exact quality of the solvent is measured by a proprietary test which expresses the solvent quality on a relative scale. This scale is called the Solvent Quality Index. While the separation of the catalyst from the liquefaction step prevents catalyst loading with ash and many other contaminants, a problem still seems to remain. This problem is that the process gives a high yield of non-volatile bottoms, which is probably due to the finite amount of transferable hydrogen that can be carried back to the reactor by the recycle solvent. As mentioned earlier, a source of hydrogen is necessary during breakdown to cap the thermally produced radicals and prevent char formation during liquefaction.

The SRC-II process does not depend on addition of any manufactured catalyst, relying instead on increased reactor residence time and a large amount of product recycle to achieve the desired degree of liquefaction. Coal ash, which has some proven catalytic activity,[14] is allowed to build up in concentration in the reactor. The process allows a large part of the preasphaltene and asphaltene product to be recycled to the reactor, thus allowing more complete breakdown of these large molecules. One of the main problems with this

process is a build-up of ash in the reactor due to the design of the reactor, thus requiring a low ash coal for operation. Another is the high viscosity and solids content of the recycle stream which causes increased abrasive wear in materials, therefore causing pump and equipment failure.(15)

The H-Coal process is different from the two above in that a catalyst is added directly to the reactor and allows intimate mixing of the catalyst, hydrogen, recycle solvent and unreacted coal, thereby allowing continual replenishing of a hydrogen-rich solvent. The main benefit of having an abundance of hydrogen at this point is that char does not form as rapidly; therefore,this process gives a high yield of light distillates. One of the main problems with this process is that the catalyst can become deactivated by becoming loaded with ash and other types of contaminants. Also, of these three processes, the H-Coal process is more likely to overhydrogenate its recycle solvent, which may be detrimental to its quality.(16)

In all of these processes, the recycle solvent is different, dependent on the reactor conditions and other engineering differences in the processes. The EDS process operates on a light recycle oil. In comparison, the SRC-II process uses a heavy recycle oil. The H-Coal process uses an intermedicate recycle oil as compared to the other two processes. However, in each case the solvent is used in much the same way.

The action or reaction of various solvents on coal has long been of interest to numerous scientists. The first attempts to break down coal used extraction by various pure organic solvents.

As early as 1860, DeMovsilly[17] extracted various coals with boiling benzene, alcohol, ether, chloroform and carbon disulfide. In 1861, Fremy[18] first used pyridine as a solvent,and in 1899 Belson[19] reported a 20% extraction yield with pyridine. In 1914, Vignors[20] obtained an approximate 50% extraction using quinoline. In the early 1900's through the 1920's Wheeler and others,[21] using pyridine as the extraction solvent, worked on compound purification and identification of the extracts. Fisher and coworkers[22] used benzene as an extraction medium, working along similar lines to that of Wheeler with the notable exception of extracting the coal under pressure. Up to this point, no attempt had been made to chemically break down or alter the coal.

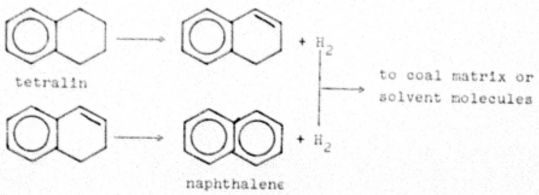
In a paper published in the late 1920's, Pan and Hadley[23] used phenol as a solvent to achieve breakdown of the coal and in the same time frame Novak and Hubacek[24] used tetralin as the primary solvent for breaking down the coal. Until 1930 most investigators supported the theory that coal extracts were colloidal systems.[25] It is interesting to note at this point that most papers dealt with the effectiveness of a solvent to solubilize coal, while hydrogenation of the coal was something usually carried out separately. However, in a paper published in 1933, Pott and Broche[26] described a process in which phenols and cresols were used as solvent media and tetralin as hydrogen donor to liquefy coal. Around 1950, Dryden[27] utilized four tests to determine the solvent power of a liquid and divided the various solvents used into five categories.[28]

It was mainly in the early 1950's and 60's that interest in the relationships of the coal and solvent system ballooned, with emphasis placed on the coal liquids to act as solvent for the parent coal, closely in parallel with the development of the previously mentioned liquefaction processes.(29)

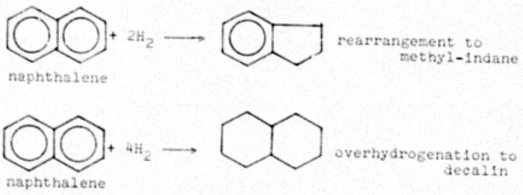
During this time, much work was put into the study of the recycle solvent. One of the main chemical characteristics of interest has been, and will be for some time yet, the hdyrogen donating capabilities of some molecules of the solvent. However, the donor capability of the solvent is not the only item that goes into the makeup of the total recycle solvent properties, since liquefaction studies carried out in tests with non-donor solvents show liquefaction of the coal matrix.

The criteria for a molecule to have the ability to donate hydrogen are not stringent. For the main donating species in the recycle solvent, the molecule requires at least one aromatic ring adjacent to at least one partially or completely hydrogenated ring, with each ring usually understood to be a six-membered ring.(30) Tetralin (tetrahydronaphthalene) is the smallest molecule that can meet these requirements and is probably the most often used example of a hydrogen donating molecule.

The general reaction is as follows.(31)



The reverse reaction, usually in a hydrogen atmosphere and in the presence of a catalyst, regenerates the tetralin. There are many groups of polycyclic compounds of varying size in a coal liquid, and many of these are capable of hydrogen transfer.(32) There are also many side reactions which are detrimental to the donor ability of the recycle solvent. Two of these reactions, shown below, give rise to products that lack hydrogen donor ability, as compared to that of tetralin. Again, tetralin is used as the example, but these reactions apply to any polycyclic molecule.(33)



In addition to the donor ability of some molecules, other properties of the recycle solvent have been studied.

These include boiling range, viscosity, aromatic vs. aliphatic content, as well as others. All of these factors contribute to the overall solvent quality of any coal liquid. Attempts are being made to correlate these observed physical and chemical properties to the values obtained when determining the solvent quality of a coal liquid. These values, although relative, may be used to help determine if a coal liquefaction plant is operating at peak efficiency.

To date, one of the most useful tests for evaluation of a recycle solvent is a direct measurement of its power to convert a coal to a liquid. The easiest and quickest way to do this is by use of a tubing-bomb reactor.[34] These small reactors, which may be called a microautoclave reactor (MA), allow for a quick turnaround time (approx. 24-36 hrs). They also allow for an accurate, if relative, idea of the quality of a recycle solvent. It is very important, when analyzing results of a solvent quality determination, to keep in mind that the numbers are relative. The numbers obtained in these tests will change with differing standard coals or reaction conditions, and especially with differing procedures, in various laboratories. However, with strict adherance to procedure, much can be learned by comparison of various solvents on the micro-autoclave.

The use of the MA for solvent testing was developed by Conoco Coal Development Company, Library, PA.[35] There are several inherent advantages in this system over the stirred autoclave batch reactor. The advantages include (1) much smaller amounts of material can be tested, (2) faster heat-up

and cool-down times, (3) no vessel internals to be concerned about, and (4) mass-transfer between solid-liquid is improved.[36]

The smaller amounts of material needed can be of great value in situations where a small solvent sample is distilled, or otherwise separated, so that various components of the sample can be tested, both for coal conversion and other types of analyses. The faster heat-up and cool-down times are due to the small size of the reaction vessel. Also the size of these vessels allows 2 or 4 of them to be run simultaneously, giving duplicates of a reaction in the same environment. The only vessel internal that can clog in an MA is the gas-charge tube, whereas with a stirred autoclave, the gas injection system, as well as the stirrer, may clog with a viscous system, and the stirrer parts are certainly harder to quantitatively clean than an MA. Mass transfer in much better in a tubing bomb reactor, as much as 25 times more between the solid-liquid as a stirred autoclave.[37]

There are two basic solvent tests run on the MA to determine the quality of a coal solvent. One is the kindtic (KIN) test, the other is the equilibrium (EQ) test. The KIN test reflects the types of hydrogen donors the differing liquids have. The EQ test indicates the concentration of hydrogen donors present. The tests differ in their reaction conditions, solvent to coal ratio and reaction time. The KIN test is run with 12 g of coal liquid and 1.5 g of coal for 10 minutes. The EQ test is run with 10 g of coal liquid and 5 g of coal for 30 minutes.[38] These tests are very useful in characterizing the difference between coal liquefaction solvent.

Even though the numbers are relative, they can be used to help optimize reaction conditions during actual plant operation to obtain a better quality recycle solvent, hence a better conversion of coal in the overall process. However, strict adherence must be paid to the microautoclave reaction conditions to give a firm basis for comparison of these numbers.

The reactor system that Ashland Petroleum Company uses to determine the relative solvent qualities of various recycle and start-up oils is based on work done at Pennsylvania State University. The MA system used by Ashland "has been shown to be repeatable, reproducible, and to obtain relative conversion data consistent with a larger scale PDU unit operated by Hydrocarbon Research, Inc." The correlation study performed by Ashland shows a 0.99+ correlation coefficient with the results obtained by Penn State, with the values obtained by Ashland being consistently higher.(39)

The purpose of this study was to follow the solvent quality (SQ) curve of two of the recycle make up streams at the H-Coal Pilot Plant at Catlettsburg, KY.

There are three main product streams that are used in the make up of the recycle oil at the H-Coal Pilot Plant. These streams consist of the Atmospheric Still Bottoms, the Vacuum Still Bottoms and the Hydroclone Overflow. Of these three product streams, the hydroclone overflow is solid at room temperature and contains solid material (ash, coal fines, etc.), whereas the other two streams are liquid at room

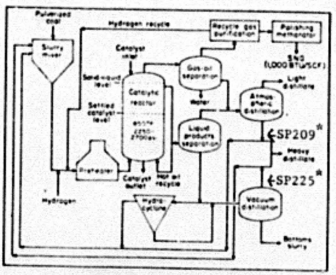
temperature. It was decided that,due to the difficulties involved in handling the Hydroclone Overflow, only the other two streams would be covered in this study.

The Atmospheric Still Bottoms is designated at the H-Coal Pilot Plant as Sample Point 209 (SP209),and the Vacuum Still Overhead is designated as Sample Point 225 (SP225). They are marked on Figure IV[40] as SP209 and SP225.

The SQ of these streams was obtained by use of a shaker-bomb liquefaction unit (the microautoclave, or MA). Correlation of the observed SQ with some of the chemical and physical properties of the recycle solvents has been accomplished. The correlation data included various elemental and physical characteristics of selected recycle oil samples, as well as HPLC separation of several of these samples.

Figure IV[40]

Schematic of Pilot Plant



II. EXPERIMENTAL

Reactor

The reactor system used in this work consists of the following subsystems.

1. A Techne SBL-2D Fluidized sand bath with a Techne TC-4B PID temperature controller. The sand bath is mounted on a travel plate with movement provided by a Parder series air cylinder pressurizable by a low pressure nitrogen source.

2. An agitation system consisting of a Reeves motodrive 052-C flow 52-450 rpm variable speed driver, with a vertical movement of 0" to 3" possible.

3. High and low pressure gas supply systems were used. The high pressure sources were a 6000 psig tank for hydrogen and a 2000 psig tank for nitrogen. These were for pressure checking of the reactors and lines before a run, charging the reactors prior to the run, and purging of the system. The low pressure systems consisted of a nitrogen supply for raising the sand bath and purging of a vacuum oven, and compressed air for fluidization of the sand bath.

4. The reactors are fabricated from 1" OD X 0.120" wall SS 316 tubing provided with swagelok SS-1610-6-16TSW tube socket weld unions and SS-1610-P plugs at each end.

A 0.25" X 0.049" wall SS 316 tube stub is welded to the center of the tube, terminating in an SS-1610XM4-P4-A-RD (2850) Whitey valve with intergral 3850 ± 150 psig rupture disk.

5. The entire unit was housed in twin Budd 60 series cabinets separated by an acrylic plastic plate.

Materials and Instrumentation

All of the solvents used in the HPLC separations were LC grade, and dried over 4-A molecular sieves overnight before use, except for the THF, which was used as received. The HPLC was a Waters Prep LC/System 500A which was used with Prepak^{TM}500/Silica columns supplied by Waters Associates. The THF used in the Soxhlet extractor and reactor washing was reagent grade with BHT added as preservative. The extraction thimbles were Schleicher and Schull extraction thimbles (25mm X 100mm).

The coal used for all MA runs was an Illinois #6 coal from the Burning Star #2 mine. This coal was furnished by Hydrocarbon Research and represents the coal feedstock used for PDU run #5 at HRI-Trenton. The coal has been stored in the crushed form since the fall of 1977 with no special procedures for oxygen exclusion. The sample of coal used for all runs on the MA had an ash value of 10.88%. The H-Coal Inventory number assigned to this coal by Ashland Petroleum Company is 20-HC-35.

The elemental analyses were performed as follows. The percent hydrogen was determined by low resolution NMR. The percent nitrogen was determined by an Antek chemical luminescence instrument. The percent nitrogen basic was determined by a potentiometric titration using acetic acid as the solvent and perchloric acid as the titrant. The ppm sulfur was determined using a Horiba X-ray florescence instrument, model number SLFA-200. These elemental analyses were run by the analytical support labs at Ashland Petroleum Company.

Sampling Protocol

The process streams at the H-Coal Pilot Plant have sampling points, which are labeled with different sample point numbers. The sample numbers for the two recycle streams which were tested, along with their names, are 209 (Atmospheric Still Bottoms) and 225 (Vacuum Still Overhead). At the time of sampling, a metal quart can was filled with the oil, and the sample point number and the time of sampling were placed on a tag and affixed to the can. These cans were delivered by courier to the H-Coal Support Group. This group ran a Sim-D (simulated distillation) and °API (density measurement) on the samples then placed them in the H-Coal storage room. From these cans, samples were obtained to do the solvent study. Copies of the analysis sheets from the H-Coal Support Group were also obtained.

A sample of four to eight ounces was taken from the cans, with sampling intervals of two to four days, depending on the operation of the H-Coal Pilot Plant. These samples

were recorded in the H-Coal inventory book of the Synthetic Fuels Group and given a number according to the sample point and order in which they were recorded. For example, a sample taken from sample point 209 would have the inventory number 209-HC-XX, with the XX progressing sequentially. After being assigned a number, the samples were run on the MA to establish their relative SG. Graphs were plotted with time as the X-axis, and containing SG, °API, IBP and 50% point data for each sample. The IBP and 50% point data were determined by Sim-D and obtained from the H-Coal Support Group. Also, the slurry mix was monitored by the H-Coal Support Group and a graph of the percent quinoline insolubles in the slurry on a daily basis was included on the graph. This provided some idea of the amount of coal going to the reactor.

Reactor Procedure

The same procedure was followed for each run. All data for the runs are recorded in either MA book number two or MA book number three, which are on file at Ashland Petroleum Company. The procedure followed is described below.

The day before a run (at least 24 hours), extraction thimbles and sufficient coal were placed in the vacuum oven to dry. The next morning, the sand bath was turned on and fluidized. Heat-up was 50°F over the run temperature of 750°F. The coal and thimbles were removed from the oven and allowed to cool to room temperature. The tare weight of each thimble was obtained. Next, one end of each reactor was

closed, and ten grams of solvent were added, using two different solvents in duplicate for the total of four reactors. Then, five grams of coal were added to each reactor, which was then sealed. All weights were measured to 0.001 grams. The reactors were mounted in the reactor assembly, then placed in the MA and connected to the carriage shaft, which provides the necessary agitation. One-eighth inch gas supply lines were connected to each reactor. The reactors were then pressure tested for leaks with nitrogen, first at 500 psig then at 1000 psig. This pressure was released, and the reactors were pressure tested with hydrogen at 1500 psig and then 2000 psig. This pressure was released and the reactors charged with 500 psig hydrogen. During this pressure testing, most of the oxygen was flushed from the reactors. After the reactors were charged with 500 psig of hydrogen, they were closed and the rest of the gas supply system was vented, then pressurized with nitrogen to 750 psig.

Agitation was then started, preset at 400 rpm and one-half inch vertical movement. The sand bath was then raised, immersing the reactors into the fluidized bed. At the end of thirty minutes, the sand bath was lowered and turned off. The pressure was released from the supply lines but not from the reactors, and the one-eighth inch gas supply lines were removed from the reactors. The reactor assembly was loosened from the carriage, and at ten minutes from the time the sand bath was lowered, the reactors in the reactor assembly were immersed, except for the valves, in cold tap water. Tap water was run into the stainless steel bucket containing the

reactors to facilitate cooling. After being cooled to room temperature, the reactors were taken from the assembly and the reactor pressure released under a hood. This was done within ten minutes after removal from the MA.

The reactor and caps were washed with THF in such a way that the contents were quantitatively transferred to separate, tared extraction thimbles. These thimbles were then placed in the Soxhlet extraction device and extracted with fresh THF for six to eight hours or until the extraction fluid from the thimbles ran clear. The thimbles were removed from the extractor and permitted to air dry, then dried in the vacuum oven for twenty-four hours. The weights were then obtained.

The conversion was calculated on a dry, ash-free basis. No correction was made for changes in mineral matter during processing. Tetralin was used as the standard for a base-line conversion determination. This conversion was determined to be 86.7% on a dry-ash-free basis. The solvent quality is calculated as follows.

$$\text{Solvent Quality (SQ)} = \frac{\% \text{ daf conversion of sample}}{\% \text{ daf conversion of tetralin}} \times 100$$

After running for several weeks, the graph of the SQ versus time was reviewed, with certain samples chosen to undergo further analysis. The criteria for this selection was to choose samples with low, medium, and high SQ so that the full range of SQ values could be checked without analyzing each solvent sample obtained. Of the samples chosen for

elemental analysis, nine were selected for separation by HPLC. This separation gave four fractions. These consisted of a saturate fraction, a one-to-three ring aromatic fraction, a three-plus aromatic fraction, and a polar and heterocyclic fraction.

These samples were run according to a write-up entitled "Water Associates Energy Project Preparative Liquid Chromatographic Technique for Hydrocarbon Group Separation of Coal Liquids,"[41] with some exceptions. These are as follows. The asphaltenes of the coal liquid were separated by dissolving the samples in 300 ml of hexane and then removing the insolubles by filtration. The hexane filtrate was removed by evaporation and then the residue was injected quantitatively onto the HPLC column. The asphaltenes were discarded after their weight had been determined. The volume of solvent two was doubled. This allowed the third peak noted on the detector to come much nearer the baseline before the next solvent front moved through, bringing with it the material comprising the fourth fraction. The pump speed after equilibration of the column was 100 ml per minute with the attenuation set at two. The sample size ranged between 7.0 - 7.5 grams. Since the columns were re-used, a standard was run before each separation to determine the activity of the column. Fractions were taken such that the peaks shown by the detector were separated.

III. RESULTS

The data presented in the following tables is the result of work done by the H-Coal Support Group at Ashland Petroleum Company, the analytical support labs at this company, and the sample processing done by the author. The following discussion is a brief description of these tables.

Table 3 gives the analysis of the slurry feed mix. The percent quinoline insoluble can be used as a measure of how much coal is being fed into the reactor. It is not an exact measure due to the ash being recycled to the slurry mix tack from the hydroclone overflow.

Tables 4 and 5 gives the physical properties of °API, IBP, 50% point, and the SQ of sample points 209 and 225.

Table 6 gives the elemental analysis for various samples chosen from each sample stream (209 and 225).

Table 7 gives all the data obtained from the HPLC separations of the selected recycle solvents from each sample stream.

Table 3

H-COAL PILOT PLANT SLURRY FEED MIX

Date	Time	% Ash	% Quinoline Insoluble
8-14-81	1750	13.8	35.6
8-15-81	1750	8.7	39.0
8-16-81	1745	7.8	37.6
8-17-81	1750	9.3	29.1
8-18-81	1735	11.6	41.8
8-19-81	0943	1.2	3.5
8-20-81	0030	.5	~1
8-21-81	0025	.5	~1
8-22-81	0135	~0	~0
8-23-81	0145	~0	~0
8-24-81	1520	3.5	23.9
8-25-81	1600	7.1	30.8
8-26-81	~1600	9.0	35.5
8-27-81	1712	7.8	40.5
8-28-81	0750	7.3	36.3
8-29-81	0750	~0	~0
8-30-81		~0	~0
8-31-81		~0	~0
9-01-81		~0	~0
9-02-81	1655	5.6	28.6
9-03-81		6.9	32.7
9-04-81	1730	8.3	32.4
9-05-81	1545	6.0	22.6
9-06-81	1545	8.2	34.4
9-07-81	1550	8.0	32.8
9-08-81	1642	8.1	36.4
9-09-81	1642	10.4	39.2
9-10-81	1600	9.0	39.0
9-11-81	1750	9.7	20.1
9-12-81	1535	9.4	37.2

Table 3 (continued)

Date	Time	% Ash	% Quinoline Insoluble
9-13-81	1560	7.7	35.0
9-14-81	1635	7.7	32.2
9-15-81	1625	7.2	32.0
9-16-81	1600	8.0	35.7
9-17-81	1520	9.1	37.7
9-18-81	1800	7.9	33.0
9-19-81	1510	7.6	36.4
9-20-81	1515	7.4	38.8
9-21-81	1520	7.0	39.5
9-22-81	1519	7.6	37.1
9-23-81	1511	6.8	40.4
9-24-81	1325	7.6	34.7
9-25-81	1545	8.3	37.5
9-26-81	1520	9.3	37.1
9-28-81	1506		
10-01-81	1830	9.9	35.2
10-02-81	1610	9.6	30.5
10-03-81	1615	9.4	32.0
10-04-81	1530	4.3	6.1
10-05-81	0740	.6	~2.0
10-07-81	1712	10.7	38.2
10-08-81	0715	6.6	
10-09-81	2320	2.9	8.6
10-10-81	1520	9.3	35.3
10-11-81	1620	9.5	38.7
10-12-81	1628	8.7	35.9
10-14-81	2310	1.5	8.6
10-15-81	1555	7.6	33.4
10-16-81	1520	8.7	32.1
10-17-81	1500	9.4	34.7
10-18-81	1500	9.7	35.6
10-19-81	1528	10.3	38.0
10-20-81	0715	10.1	24.0

Table 3 (continued)

Date	Time	% Ash	% Quinoline Insoluble
10-21-81	0720	0.8	~4.0
10-23-81	1510	9.0	29.2
10-24-81	1505	9.6	37.5
10-25-81	1510	10.0	43.5
10-26-81	1535	10.0	35.6
10-27-81	1520	9.3	35.4
10-28-81	1526	9.3	35.3
10-29-81	1505	9.7	36.6
10-30-81	1540	10.5	34.8
10-31-81	1510	9.9	37.3
11-01-81	1512	10.3	36.6
11-02-81	1509	10.4	35.4
11-03-81	1510	9.2	33.2

Table 4

SAMPLE POINT 209 - PHYSICAL PROPERTIES AND SQ

Date	Sample #	Time	API	Distribution IBP	Distribution 50%	Solvent Quality	
8-14-81	209-HC-14	2030	14.5	454	604	82.75	81.92
8-16-81	209-HC-15	1735	13.8	457	601	82.53	84.08
8-20-81	209-HC-19	19.2	19.2	471	571	86.88	87.38
8-22-81	209-HC-20	0141	19.9	483	579	88.40	86.03
8-25-81	209-HC-16	1755	18.2	444	584	76.44	75.97
8-26-81	209-HC-17	1745	17.5	412	574	76.19	77.27
8-27-81	209-HC-18	2030	15.7	421	578	83.64	82.65
8-28-81	209-HC-22	0940	17.8	222	554	80.85	76.37
9-02-81	209-HC-21	~0900	17.9	445	599		76.25
9-04-81	209-HC-23	0040	15.7	428	567	77.44	77.68
9-05-81	209-HC-24	2324	15.6	414	541	76.94	77.54
9-07-81	209-HC-25	2326	13.8	424	549	87.61	87.44
9-11-81	209-HC-26	2325	12.7	431	575	85.54	
9-16-81	209-HC-27	0735	10.9	449	577	91.52	91.76
9-20-81	209-HC-28	2325	9.7	439	575	88.78	88.47
9-24-81	209-HC-29	2310	10.3	443	570	88.56	89.97
9-28-81	209-HC-30	0720	16.9	440	585	87.10	87.82
10-01-81	209-HC31	0723	17.7	428	581	70.83	72.09
10-06-81	209-HC-32	0145	19.2	428	554	72.51	73.81
10-10-81	209-HC-33	0455	17.9	411	572	71.07	73.53
10-13-81	209-HC-34	2305	17.9	422	549	74.00	76.14
10-18-81	209-HC-35	0415	12.4	413	568	87.13	88.72
10-22-81	209-HC-36	0930	18.7	394	551	86.20	84.37
10-25-81	209-HC-37	2300	13.3	425	560	83.87	83.47
10-30-81	209-HC-38	0120	10.5	458	579	87.13	86.45

Table 5

SAMPLE POINT 225 - PHYSICAL PROPERTIES AND SQ

Date	Sample #	Time	API	Distribution IBP	Distribution 50%	Solvent Quality	
8-14-81	225-HC-01	1720	11.5	422	656	84.69	87.85
8-16-81	225-HC-02	1750	6.6	406	658	91.53	91.94
8-25-81	225-HC-03	1730	16.8	440	592	71.22	72.33
8-26-81	225-HC-04	1758	10.3	487	655	87.61	89.07
8-27-81	225-HC-05	1010	8.0	499	669	94.27	93.47
9-02-81	225-HC-07	0125	18.3	419	582	80.47	79.24
9-04-81	225-HC-09	0120	8.5	449	647	93.82	92.66
9-06-81	225-HC-10	0135	9.3	389	585	86.22	87.78
9-08-81	225-HC-11	0135	5.7	391	605	90.96	90.98
9-12-81	225-HC-12	0135	11.1	440	578	90.72	88.43
9-16-81	225-HC-13	0125	9.6	431	574	93.21	90.80
9-20-81	225-HC-14	0125	8.9	405	576	89.76	89.72
9-24-81	225-HC-15	0715	9.8	445	614	90.81	93.54
9-28-81	225-HC-16	1515	13.0	329	568	92.06	93.72
10-11-81	225-HC-17	0840	20.4	206	509	79.33	80.99
10-18-81	225-HC-18	0755	22.1	189	457	72.82	71.64
10-22-81	225-HC-19	0914	16.8	274	552	80.21	80.08
10-26-81	225-HC-20	0125	17.8	242	505	74.88	71.14
10-29-81	225-HC-21	2358	8.5	417	577	89.13	90.23

Table 6

ELEMENTAL ANALYSIS OF SELECTED SOLVENT SAMPLES

Sample Number	Hydrogen % wt	Nitrogen % wt	Basic Nitrogen % wt	Sulfur PPM wt
		Sample Point 209		
14	10.17	.31	.22	751
20	11.10	.07	.04	232
16	10.79	.14	.10	590
18	10.31	.27	.20	1127
21	10.84	.10	.06	624
24	10.10	.30	.22	1491
27	9.33	.48	.34	1292
30	10.71	.18	.12	500
31	10.78	.14	.09	700
34	10.57	.20	.14	600
37	9.79	.55	.37	1400
		Sample Point 225		
01	9.76	.32	.21	855
02	8.89	.60	.38	1221
03	10.95	.15	.11	535
05	9.15	.44	.27	1124
10	9.10	.45	.28	1470
13	9.33	.53	.36	1410
16	9.86	.40	.27	754
17	10.61	.23	.18	1200
21	8.98	.68	.44	1400

Table 7

HPLC SEPARATION OF SELECTED H-COAL LIQUIDS

S.P. Number	Solvent Quality		F-1 Wt %	F-2 Wt %	F-3 Wt %	F-4 Wt %	Asphaltene Wt %	Percent Recovered	Sample Wt
225-HC-10	86.22	87.78	14.47	54.98	9.17	22.03	1.25	101.90	7.466
225-HC-16	92.06	93.72	13.61	70.63	4.08	13.42	.51	102.95	7.258
225-HC-17	79.33	80.99	29.79	49.33	3.83	18.73	.07	100.75	7.069
225-HC-21	89.13	90.23	11.15	60.96	4.78	28.25	1.43	106.57	7.238
209-HC-24	76.94	77.54	24.11	59.22	4.13	13.17	1.48	102.22	7.113
209-HC-30	87.18	87.82	29.55	69.52	2.45	5.73	.42	107.67	7.138
209-HC-31	70.83	72.09	18.45	75.62	1.20	3.92	.44	99.63	7.112
209-HC-34	74.00	76.14	24.53	67.87	2.44	5.78	.15	100.77	7.145
209-HC-37	83.87	83.47	18.15	58.36	3.99	18.26	1.10	99.86	7.260

IV. DISCUSSION

Let us begin the examination of the data by obtaining an overview of the period when samples were taken from the H-Coal Pilot Plant. This data is best summarized in Figures V and VI, which show several of the physical properties of the recycle oils, as well as their solvent quality, on a plot against time. These physical properties are defined as follows. The IBP and 50% are terms from a simulated distillation (Sim-D) of the recycle oil. This is done on a gas chromatograph (GC) which is calibrated to show the relative boiling point of the sample. The IBP is the initial boiling point of the recycle oil as first picked up by the detector. The signal from the detector is printed as a curve on a strip chart recorder and the area under the curve is integrated to give the 50% temperature. This is the point at which, by the integrated area under the curve, one-half of the injected sample has passed through the GC. Using the GC for this distillation is a very fast and efficient way to process large numbers of samples.

The other property, the °API, is an inverse density measure. The °API of water is 10, and it is an inverse measure in that if the °API is greater than 10, the substance is less dense than water, and if it is less than 10, it is more dense than water.

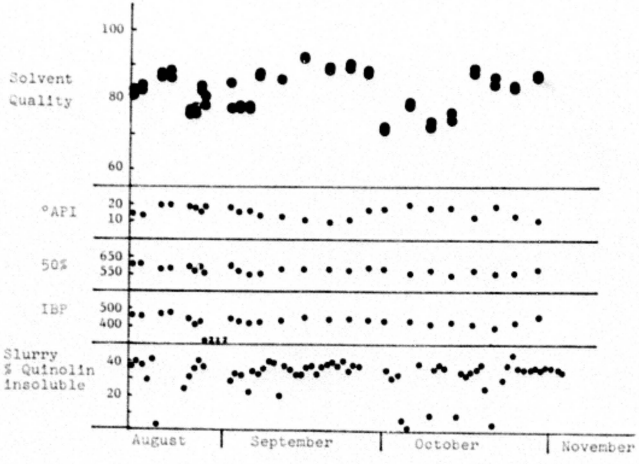


Figure V. Atmospheric Still Bottoms - S.P. 209

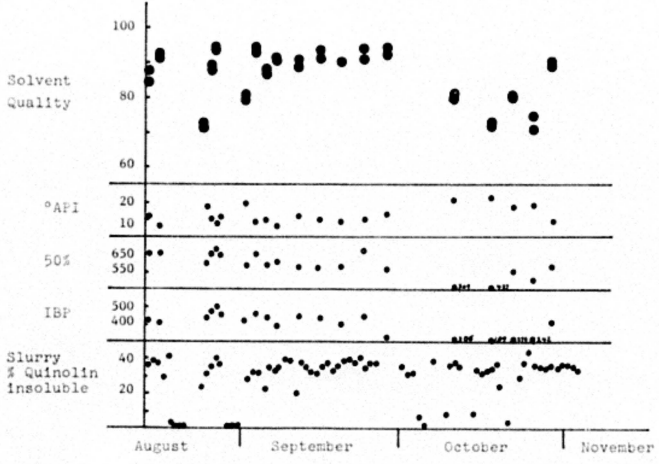


Figure VI. Vacuum Still Overhead - S.P. 225

These graphs also show the amount of quinoline insoluble material in the slurry feed on a daily basis. This is determined by taking a sample from the reactor feed, which is made up of the coal going into the reactor, as well as the blend of the recycle streams used to suspend this coal. The insoluble portion of this will basically consist of the coal being fed into the reactor and the ash and fines contained in the recycle blend from the hydroclone overflow. The majority of the quinoline insoluble material is made up of coal, so this number is used as a relative measure to determine if the coal feed rate was constant, fluctuating or nill.

It is very important to know if the reactor was converting coal when the samples were taken. The quinoline insolubles made up between 30-40% of the slurry feed most of the time the plant ran, indicating a steady supply of coal being fed into the reactor. This measurement is seen to drop to zero when the plant was off coal and slowly rise to between 30-40% again as the plant was placed back on coal. This can affect the sample character drastically, because when the plant is off coal, the product is being recycled at a much larger rate than usual. This can lead to an overhydrogenation and cracking of the recycle solvent. Also, a make up solvent may need to be added at these times to maintain solvent balance, due to no new product being formed from coal. This make up solvent is very different from the coal-derived solvent, and can lead to erroneous conclusions if not taken into consideration. Therefore, the remainder of the graphs in this thesis

will consist of two types of data. Those data points that deal with samples taken while the plant was operating with coal will be represented with a solid figure, while the data points obtained from samples taken during the fluidations of the plant will be represented as an outline figure. The main discussion and conclusions will be drawn from the points while the plant was on coal, with off coal points being considered too variable from which to draw any valid conclusions.

With the solvent quality being the key factor in the interpretation of the results, most of the following graphs are plotted against this value, with SQ being the dependent, or Y, value. First we shall compare the SQ with the physical characteristics of the various recycle solvent samples obtained. The first property is the IBP and 50% points obtained from the Sim-D. These points are graphed on Figures VII (SP 209) and VIII (SP 225).

The graph for SP 209 shows an IBP range for the on-coal points of 411°F to 457°F except for one sample which had an IBP of 222°F. The 50% range is 549°F to 604°F. The small ranges of these boiling points indicate a consistency in fractionation. However, there does not seem to be any tie-in between the SQ and these boiling points as the correlation coefficient for both data sets is <.2.

The graph for SP 225 shows an IBP range for the on-coal points of 189°F to 499°F and for the 90% points a range of 457°F to 669°F. These ranges are much larger than those of the SP 209 samples and reflect a differing fractionator performance. In addition to this, these samples show a strong

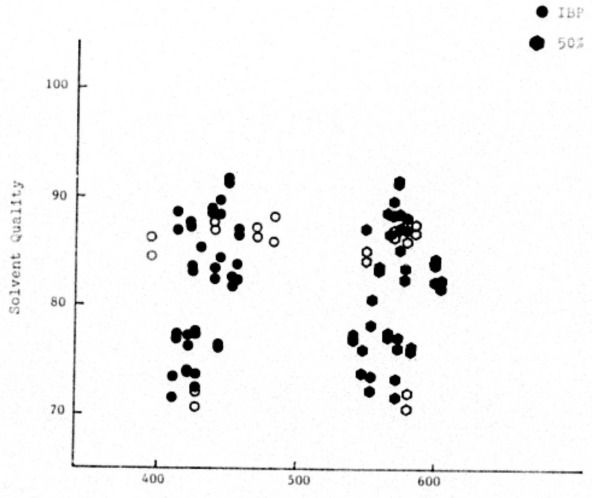


Figure VII. Fractionator Performance - S.P. 209

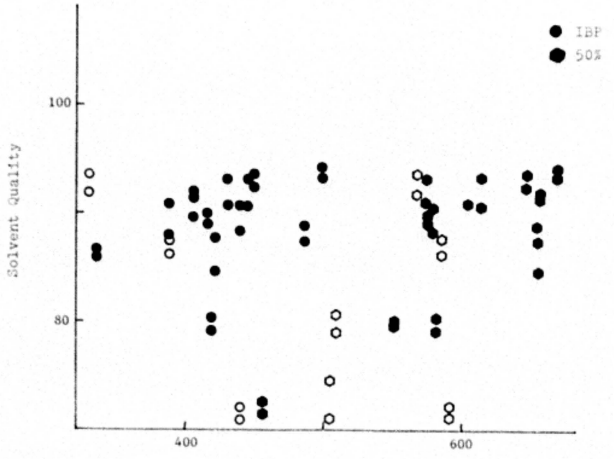


Figure VIII. Fractionator Performance - S.P. 225

relationship between these boiling points and the observed SQ. The IBP shows a correlation coefficient of .822 and the 50% point .761, demonstrating a high degree of certainty that these data are related.

This relationship is a very simple one that is related to the large range of boiling points. It is well known that the better donor solvents are polynuclear units and by their size would have larger boiling points than other coal matrix fragments produced in the breakdown of coal. These smaller, non-donor fragments would act as a dilutant to the solvent quality of the overall recycle solvent, giving an impression that the boiling point has a direct impact on the solvent quality. The boiling point does not have a direct effect on the solvent quality, but an indirect effect by helping to control the types of molecules in the recycle stream.

The next property to be discussed is the °API. In figures IX and X are graphed the °API for SP 209 and SP 225, respectively. The on-coal points in SP 209 show a range of 9.7 to 19.2 °API and have a correlation coefficient (V) of -.926. The on-coal points in SV 225 have a range of 6.6 to 22.1 °API and a V value of -.949. Both of these sample points therefore show a 99.9%+ degree of certainty that the data is related, with the negative sign of the V value showing that it is an inverse relationship. This can best be explained as the effect of polynuclear aromatics, which are the better hydrogen donor molecules, having a greater density than the saturate compounds.

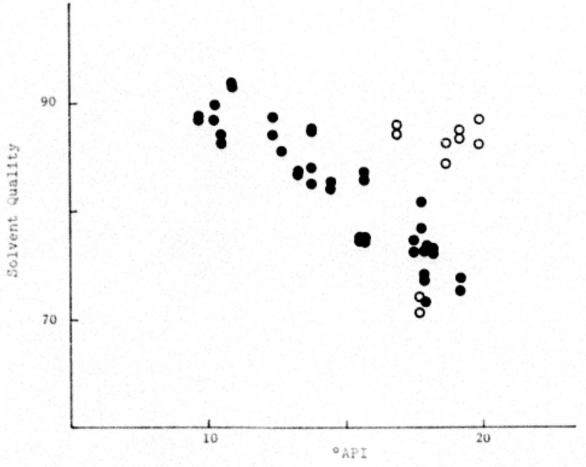


Figure IX. Solvent Quality Density Dependence - S.P. 209

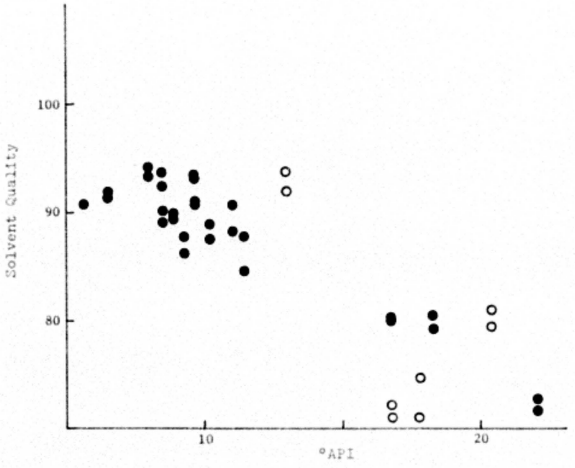


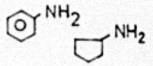
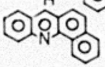
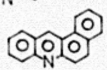
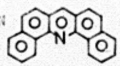
Figure X. Solvent Quality Density Dependence - S.P. 225

The next section of this thesis deals with the elemental analysis of the recycle oils. As stated previously, only a select number of the recycle solvents were analyzed. Of the nine off-coal samples listed previously, elemental analysis data were collected on only six. The remaining data is taken from on-coal samples. In dealing with the analysis of this data, a decision was made to disregard the data points from the off-coal samples when establishing the relationships between the data and the trends that are shown by it. This allows the trends shown from the on-coal samples to be dealt with on their own merits. This also allows better generalization of the data obtained with the operation of the pilot plant while the plant was on continuous operation. However, the off-coal data points should not be totally ignored because they give an idea of what happens during fluctuations in coal usage.

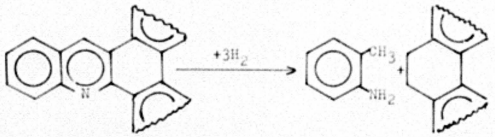
It has been shown that as the recycle oil of a coal conversion plant is hydrogenated to a greater degree, the hetercatom content is reduced.[42] This is observable in the data of this thesis, as well as other factors influencing the elemental content of the recycle oil. A short discusion of the HDN and HDS processes is given below due to its relevance to the data concerning the heteroatom content of the recycle oils in this thesis. First let us examine the nitrogen heteroatomic species which have been found in coal liquids. Some examples of these compounds are listed in Table 8.[43] All of these compounds may be derived from the coal matrix. Most of the aromatic compounds have methyl and alkyl

Table 8

SOME COMMON NITROGEN COMPOUNDS FOUND IN COAL LIQUIDS

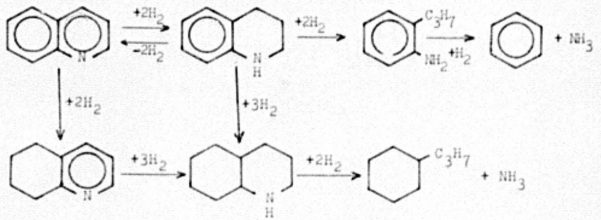
Compound	Formula	Structure
Nonheterocyclic compounds:		
Aniline	$C_6H_5NH_2$	
Pentylamine	$C_5H_{11}NH_2$	
Nonbasic heterocyclic Compounds:		
Pyrrole	C_4H_5N	
Indole	C_8H_7N	
Carbazole	$C_{12}H_9N$	
Basic heterocyclic compounds:		
Pyridine	C_5H_5N	
Quinoline	C_9H_7N	
Indoline	C_8H_9N	
Acridine	$C_{13}H_9N$	
Benz(a)acridine	$C_{17}H_{11}N$	
Benz(c)acridine	$C_{17}H_{11}N$	
Dibenz(c,h)acridine	$C_{21}H_{13}N$	

substituents due to the fragmentation process of the coal matrix during liquefaction. An example of this process is given below.[44]



The mechanism for the HDN process has been described to consist of three steps. These are: 1. Rapid hydrogenation of aromatic and heterocyclic rings, 2. Slow ring rupture at the C-N bond, and 3. Rapid denitrogenation resulting in parafins (or olefins) and NH_3.(45)

An example of the HDN mechanism is given below.(46)



It may easily be seen in this example that a large input of hydrogen is necessary for the nitrogen removal. Another factor which has been proven is that this process is difficult, and the saturation of the heterocyclic ring is required before ring scission may occur.(47)

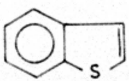
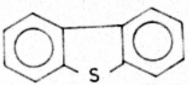
Next let us examine the HDS process. Some examples of the sulfur containing species found in coal liquids are given

in Table 9.[48] As with the nitrogen containing species, these may also have various side chains. The sulfur atom is easier to remove from the coal liquid than the nitrogen atom. This can be seen in the bond strengths listed in Table 1. There is also a large difference in the mechanism of sulfur removal compared to that of nitrogen removal. In work with dibenzothiophene, it was found that "the reaction involves direct sulfur extrusion with greater than 95% selectivity."[49] This means that, compared to HDN, which usually requires complete ring saturation, the HDS process is more likely to split the sulfur out without saturation of the heterocyclic ring system first. This means that the HDS process requires less hydrogen than a similar HDN reaction. This also leads to the conclusion that there will be a larger percentage of the total sulufr removed than the total nitrogen.

In the following graphs dealing with the elemental analysis, the sample points from the two differing sample streams are graphed together. Figure XI shows the Solvent Quality graphed versus the percent hydrogen and ppm sulfur of the recycle oil. Let us first ecamine the graph dealing with the SQ versus the %H in the recycle oil samples. It is seen from the solid points that there is an increase in the solvent quality as the %H decreases. These data have a correlation coefficient of -.929, demonstrating a close relationship between these parameters. This general trend was also detected in the work done by Ashland Petroleum Company on some of the PDU (process development unit) samples

Table 9[48]

SOME COMMON SULFUR COMPOUNDS FOUND IN COAL LIQUIDS

Mercaptans	RSH
Disulfides	RSSR'
Sulfides	
Thiophenes	
Benzothiophenes	
Dibenzothiophenes	

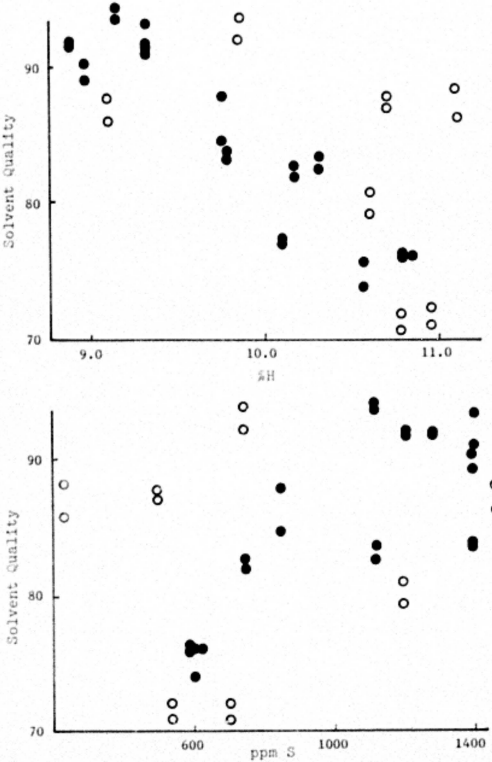


Figure XI. Elemental Analysis - %H, ppm S

from HRI-Trenton.[50] This point is very important, in that it shows that the design scale-up was successful from the PDU to pilot-plant stages. The decrease in the SQ as the hydrogen content increased can be explained as an over-hydrogenation of the recycle solvent. This gives fewer good hydrogen donor fragments as the hydrogen content of the recycle solvent is increased.

From this same graph the samples taken during fluctuation in coal usage show some solvent qualities that are higher than their %H would indicate, and some lower. Upon examination of the quinoline insoluble graph from Figure III, it can be seen that the data points that have a relatively high solvent quality for their hydrogen content were taken as the H-Coal Pilot Plant was going off coal. Conversely, each of the lower solvent quality samples was taken as the pilot plant was being brought back on coal. These effects could reflect the degree to which the recycle solvent has been hydrogenated, with work done by Ashland Petroleum Company showing that a recycle solvent can be underhydrogenated, thereby not reaching its full solvent potential, or overhydrogenated, thereby destroying the hydrogen donor characteristics of the molecules.[51] However, with no knowledge of the quantity of quality of make-up solvent that could have been added to the reactor during these times of coal fluctuation, any conclusions drawn about the extent of hydrogenation of the recycle solvent would be speculative.

The lower part of Figure XI shows the SQ versus the ppm S of the recycle solvent. This graph shows much scattering

and has a positive correlation coefficient of .586. This is not nearly as high as the coefficient for the %H graph, but still shows a good statistical relationship between these two values. Since the sulfur, as stated earlier, is easier to remove from the recycle solvent than other heteroatom species, part of the scattering in this graph could be due to the fluctuations in reactor conditions as the amount of coal being fed to the reactor varied, or as various amounts of make-up solvent had to be added due to no coal being added to the reactor.

Figure XII gives the solvent quality versus both the $\%N_{total}$ and the $\%N_{basic}$, respectively. The data on the graph for the $\%N_{total}$ gives a correlation coefficient of +.813, showing a strong statistical relationship between the SQ and the $\%N_{total}$. This graph seems to peak around .45% N_{total} and then decrease slightly. This may be a real decrease, or it could be from scattering of the data. There are not enough points to the right of this peak to be sure. However, if this were a real peak, it could correlate with the extent of hdyrogenation the recycle solvent has undergone. The heteroatom concentration of a recycle solvent can be related to the extent of hydrogenation the solvent has undergone, with the heteroatom content decreasing as the degree of hydrogenation is increased.(52) More work needs to be done to clarify this point.

The lower half of Figure XII shows the SQ vs. the $\%N_{basic}$. This graph shows an increase in solvent quality with increasing $\%N_{basic}$ content, with a correlation coefficient of +.783.

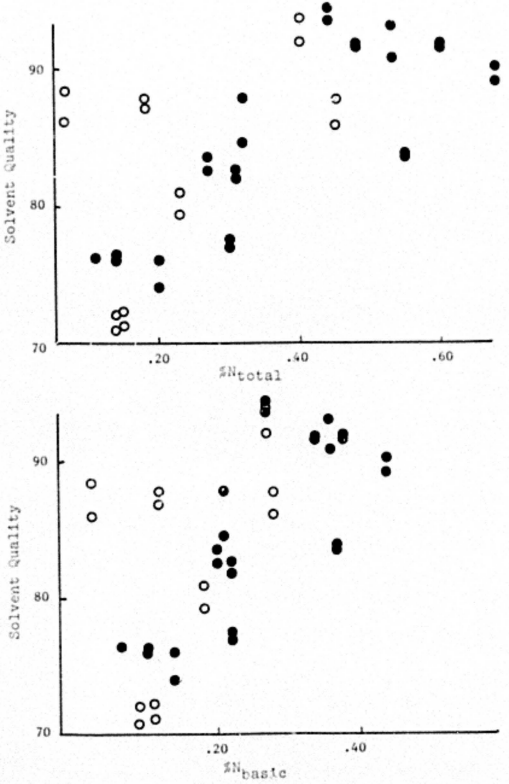
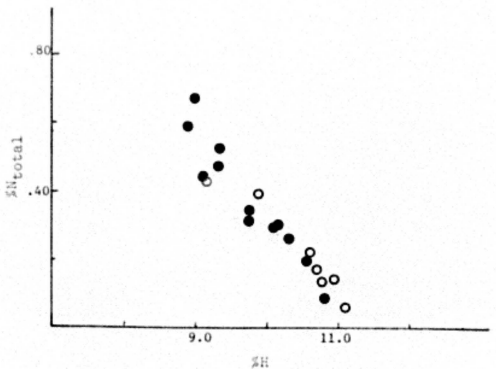


Figure XII. Elemental Analysis - $\%N_{total}$ $\%N_{basic}$

This shows a strong statistical relationship between these numbers. It is also very interesting to note that, when the $\%N_{total}$ and $\%N_{basic}$ are compared for the same data points, there is little difference between the numbers at the low nitrogen concentrations. These differences get larger as higher nitrogen levels are reached, indicating that as the recycle solvent is hydrogenated to a greater degree, the nitrogen containing species that are not basic (i.e. neutral) are removed preferentially.

As stated earlier, there is a relationship between the degree of hydrogenation of a recycle oil and its heteroatom content. By using the hydrogen content of the recycle oil as a relative means of determining the degree of hydrogenation, one can readily see how close this relationship is. In Figure XIII is graphed the $\%N_{basic}$ and the $\%N_{total}$ vs. the %H. Both of these graphs show very little scattering and very high correlation coefficients. The coefficients for the $\%N_{basic}$ vs. %H is -.906, and for the $\%N_{total}$ vs. %H is -.930. These both show a very strong statistical relationship between the determined values, and interestingly do not show much deviation, even in the samples taken during the coal usage fluctuation at the pilot plant.

Graphed in Figure XIV is the ppm S vs. the %H. Again, there is a very good statistical relationship represented, with the correlation coefficient being -.713. This graph shows more data scattering than the $\%N_{basic}$ and $\%N_{total}$



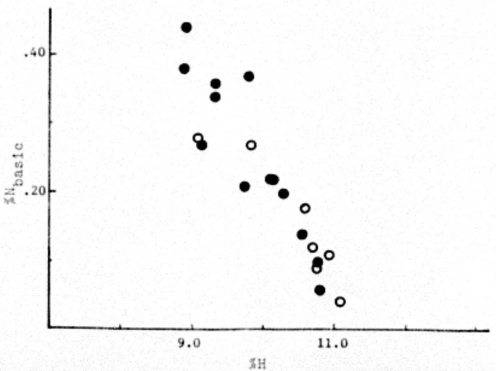


Figure XIII. Correlation of $\%N_{total}$, $\%N_{basic}$ with %H

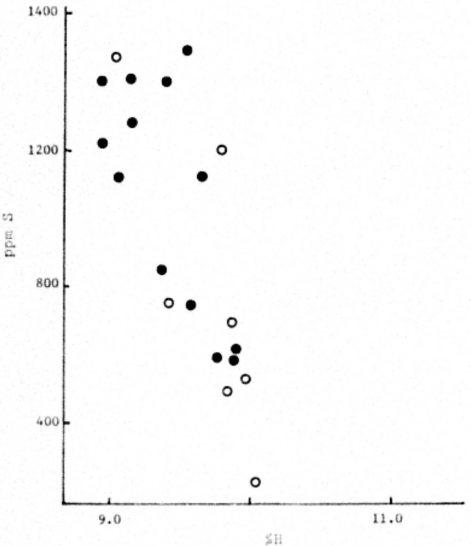


Figure XIV. Correlation of ppm S with %H

versus %H graphs, which is probably due to the sensitivity of the sulfur removal to the reactor conditions, as previously mentioned.

V. HPLC DISCUSSION

Finally, to obtain some idea of the compound types in the recycle solvents, a few of the recycle solvent samples were chosen to undergo separation by HPLC. An example of the type of separation obtained from this procedure is recorded in Figure XV. Here it can be seen that a standard was run first, to determine the activity of the column. If the column gave good separation of the standard (determined visually from the strip chart), then the sample was injected onto the column in the manner previously described.

The four fractions given by this separation are described below. Fraction one was a clear liquid fraction containing the saturate compounds of the coal liquid. Fraction two was a yellow, transparent liquid containing the one to three ring aromatic compounds of the coal liquid. Fraction three was an extremely dark-brown substance, being very viscous and sometimes containing small solid particles. This fraction contains the three plus ring aromatic compounds of the coal liquid. Fraction four was a very dark-brown to black substance, being extremely viscous, but not solid. This fraction contains the polar and heterocyclic compounds of the coal liquid. Although no analyses were run on these samples, other work at Ashland Petroleum Company with similar separations demonstrated that the separation technique gave good separation of the compound types represented in the coal liquids.

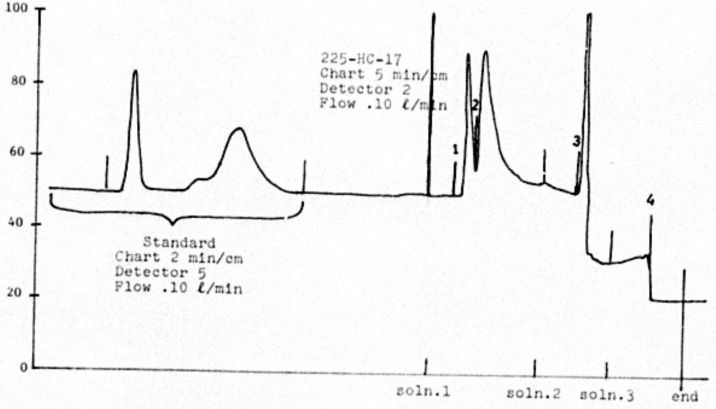


Figure XV. Sample HPLC Separation Strip Chart.

After separation of the selected samples was complete, the weight percent of each fraction was graphed against the SQ of the parent liquid. Of these fractions, only fraction one and fraction four demonstrated a correlation between their weight percent and the SQ of the parent liquid. In Figure XVI the SQ versus the weight percent of fraction one is graphed. The correlation coefficient, again of the samples taken only while the plant was steadily converting coal, is a very high -.996. This gives a very strong statistical relationship between the SQ and the wt.% of fraction one. As the wt.% of fraction one increases, the SQ decreases. This is very reasonable as fraction one is composed of the saturated compounds of the recycle solvent. These compounds are known to have little, if any, hydrogen donating ability.(53) This would mean that these compounds act primarily as a diluent of the solvent powers of the recycle solvent. The same relationship was observed in the work done by Ashland Petroleum Company on samples of the recycle solvent used from the PDU run at HRI-Trenton.(54)

The other fraction that gave a good correlation between the SQ and its weight percent was fraction four, the polar and heterocyclic fraction of the recycle oil. This can be seen in Figure XVII. The correlation coefficient is +.978, showing an increase in the SQ as the weight percent of fraction four increases. This relationship may be explained as an effect of the degree of hydrogenations on the recycle solvent. Due to the fact that this fraction concentrates the

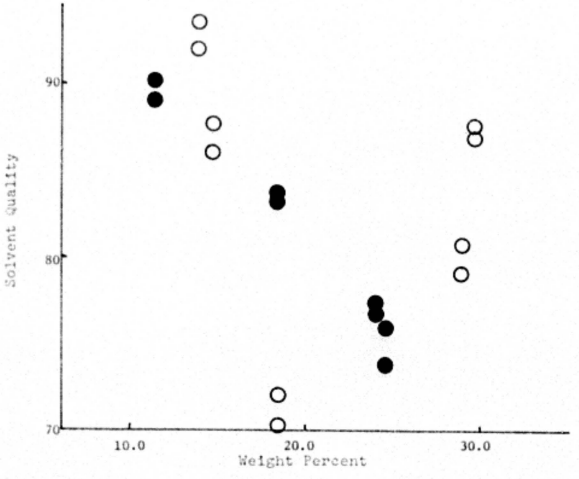


Figure XVI. HPLC Fraction 1

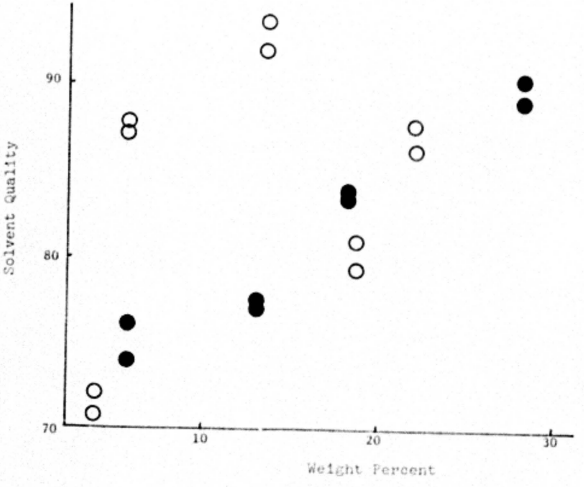


Figure XVII. HPLC Fraction 4

heteroatoms of the recycle solvent, it is more subject to change as the solvent is hydrogenated to differing degrees. As has previously been shown, as the hydrogen content of the recycle oil is increased, the heteroatom content is decreased. This may be taken to mean that the samples on the left of the graph are more hydrogenated than the samples on the right. Due to the lower values of the SQ incurred on the left of the graph, this infers that these samples have been overhydrogenated, therefore loosing some of the donor sites necessary for hydrogen transfer.

VI. CONCLUSIONS

There are several conclusions that can be drawn from this study. One is that the microautoclave, or shaker-bomb reactor, is a very effective method of determining the relative solvent quality for the recycle solvents, allowing quick return of the necessary data.

Pertaining to the data, several conclusions can be reached. One is that, of the physical properties of the recycle solvents measured, the one with the best correlation with the observed solvent quality is the °API. This measurement is easily made and reasonably dependable when applied carefully in the narrow bounds of this study.

The measurement of the heteroatom and hydrogen content can lead to a better understanding of the processes involved in the reactor when used in conjunction with the solvent quality measurements. The recycle solvent reached a peak solvent quality at about 9% hydrogen, and from this level the solvent quality decreased as the hydrogen content increased. Since most of the samples taken were above this 9% hydrogen content, this may be taken to mean that the H-Coal Pilot Plant is more likely to overhydrogenate its recycle solvents than to underhydrogenate them. The degree of hydrogenation was found to be paralleled by a reduction in the $\%N_{total}$, $\%N_{basic}$ and ppm S in the recycle solvents. It is also interesting to

note that the nonbasic nitrogen seemed to be removed preferentially to the basic N.

Another factor that seems to be important is the saturate compounds in the recycle solvent determined by HPLC analysis. These compounds seem to have no effects on the coal breakdown other than that of diluting the hydrogen donor species in the recycle solvent. If some separation shceme could be devised for on-line reduction of these compounds from the recycle stream, this would help upgrade the recycle stream and perhaps make for more efficient coal conversion. In addition to the saturated compounds, the heterocyclic fraction (Fraction 4) from the HPLC separation, which concentrates the heteroatom species, might be used as a way to determine the extent of hydrogenation of the recycle solvents. The saturate fraction and heterocyclic fraction along with other parameters, such as solvent quality, might be developed into a fast test to check and adjust the plant processes for an optimum hydrogenation of the recycle solvent.

It is the author's opinion that coal liquefaction will become increasingly important as the world oil supple decreases. A very good start in developing the necessary technology has been made, and even more effort is needed if use of coal is to play a part in meeting energy needs in the near future. To accomplish this task, research into the liquefaction processes must be done, involving all steps, from the construction of the plant to the chemistry of the reactions involved. If support for this research is provided, there is no reason that coal cannot become a viable energy alternative.

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